# (Supporting Information) Is the Solid Electrolyte Interphase an Extra-Charge Reservoir in Li-ion Batteries?

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## Methods

#### 0.1 Electrodes preparation

Electrodes were fabricated using carbon coated  $ZnFe_2O_4$  particles with average dimension of 50 nm (See figure S1). The particles of carbon coated ZFO agglomerate and form microparticles in range of tens of micrometers which are the ones coming to a direct contact with the electrolytic solutions. The solid electrolyte interphase is formed on these micro structures. X-ray diffraction shows similar structure of the particles before and after carbon coating (See figure S2) and confirms that the carbon coating does not modify the structure. The presence of carbon only enhances the electronic transport while facilitates the formation of micro clusters enhancing the functionality of the electrode.

ZnFe<sub>2</sub>O<sub>4</sub> carbon-coated (ZFO-C) electrodes were prepared by using Sodium-Carboxy-Methyl-Cellulose (Na-CMC, Sigma-Aldrich) dissolved in deionized water (5:95 w/w). ZFO-C and Super-P carbon (MMM-Carbon), previously mixed and grounded in an agate mortar, were added to the binder solution and the resulting slurry was stirred for 5 h with magnetic stirrer. The mixture was stratified on Cu foil (whose thickness is 10  $\mu$ m; the surface was first wetted with acetone and scraped off with sandpaper) through Doctor Blade technique and the thickness was set to 100  $\mu$ m. The obtained layer was dried at room temperature for 30 minutes and in oven at 55°C overnight. Then the layer was pressed by Roll Press until getting a uniform thickness.

Circular electrodes with a diameter of 9 mm and a surface area of 0.636 cm<sup>2</sup> were cut and dried overnight at 120 °C under vacuum, for both ZFO-C active materials. The capacity of ZFO-C electrodes has been calculated considering a specific theoretical capacity of 1000  $mAhg^{-1}$ .<sup>1</sup> Electrochemical measurements have been carried out by using three electrode T cells (Swagelock type), by using ZFO-C electrodes as working electrode and metallic lithium as counter and reference electrodes. A glass fiber (Whatman GF/A) has been used as separator and a solution of LiPF<sub>6</sub> in EC:DMC 1:1 v/v has been used as electrolyte. All the cells have been assembled in a dry-box filled with Ar.Each sample was stopped at its specific potential point, disassembled and washed with dimethyl carbonate (DMC) to remove electrolyte impurities and residuals and then were introduced to the experimental chambers in an inert environment specified for each measurement.



Figure S1: SEM images of the carbon coated ZFO particles showing their uniform almost identically shaped particles covered with conducting carbon. On the other hand the particles form micro structures attaching together which will be in contact with the electrolytic solution.

### 0.2 Electrochemical measurements

Based on previous electrochemical results of the SEI evolution,<sup>1-3</sup> samples for ex-situ XAS analysis have been prepared by submitting ZFO-C electrodes to selected Li uptakes by GITT, specified in Fig.1a. These specific points correspond to capacity and potential values of the electrodes that underwent ex-situ XAS characterizations. First Point obtained at E=1.02



Figure S2: XRD pattern of the nanoparticles before  $(ZnFe_2O_4)$  and after carbon coating  $(ZnFe_2O_4-C)$ . The reference for spinel  $ZnFe_2O_4$  (JCPDS card No. 00-022-1012) is shown in the bottom.

V and Q=83 mAhg<sup>-1</sup> is related to the beginning of Li uptake by ZFO-C and limited SEI formation is expected. Second and third points obtained respectively at E=0.87 V, Q=167 mAhg<sup>-1</sup> and at E=0.79 V, Q=417 mAhg<sup>-1</sup>, correspond to the beginning and ending of a potential region where most of SEI formation commonly occurs. Fourth point (point D) was obtained at E=0.5 V and Q=836 mAhg<sup>-1</sup> and the last pointy at cut off potential E=0.015 and Q=1320 mAhg<sup>-1</sup> corresponding to the end of lithiation process. Delithiation points were taken at at E=1.4 V,Q=1456 mAhg<sup>-1</sup> and E=2 V, Q=1929 mAhg<sup>-1</sup> and E=3 V, Q=2131 mAhg<sup>-1</sup> corresponding to the middle and end of the delithiation process, respectively.

#### 0.3 X-ray absorption spectroscopy

We carried out our XAS experiments using radiation at the exit of the 8.1 bending magnet of the ELETTRA synchrotron facility in Trieste (Italy) (BEAR end-station BL8.1L).<sup>4</sup> The spectral energy was calibrated by referring to C  $1s-\pi^*$  transitions. The incident light was horizontally polarized and the incidence angle of the light with respect to the sample surface plane was kept fixed at 10° with the "S" polarization. High-quality soft XAS experiments on the electrodes were performed with special care during the preparation of samples. Electrodes were disassembled and dried in an Ar atmosphere and kept in sealed packs while transported to the measurement chambers. Then the samples were placed in the chambers in an argon controlled ambient. XAS measurements were done in total electron yield (TEY) and total florescence yield (TFY) modes and normalized to the incident photon flux. The total electron and total fluorescence yield techniques can have effective probing depths of around 2-10 nm and 50-100 nm, respectively.

#### 0.4 X-ray photoemission spectroscopy

For in house XPS the samples were introduced from the glove-box via a specially designed load lock chamber in the Ar ambient to avoid the moisture /air exposure of samples during transfer. The measurement were carried out using a focused monochromatized Al K<sub> $\alpha$ </sub> radiation ( $h\nu = 1486.6$  ev) with the chamber pressure of  $\sim 10^{-9}$ . Distinct points on each sample were scanned with short dwell time to confirm homogeneity of the sample as well as radiation degradation prevention. Core peaks were analyzed using a non linear Shirley background while a floating weighted least square fittings (70-80% Gaussian and 20-30 % Lorentzian) were used for the peak positions and areas. Average quantifications were considered using the cross section relative intensities I, given by

$$I_j = \frac{A_j / \sigma_j}{A_i / \sigma_i} \tag{1}$$

where A is the detected peak area and  $\sigma$  is the Scofield photo-ionization cross section.

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